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Effect of Ageing on Shape Memory Effect and Transformation Temperature on Cu-Al-Be Shape Memory Alloy

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Abstract

Cu-Al-Be ternary alloy are prepared by ingot metallurgy route. Thermal ageing of Cu-Al-Be shape Memory Alloy at different temperatures are carried out at various temperatures. The influence of ageing at a temperature above A_f (Austenite phase finish temperature) was studied and time dependency of variation in the transformation temperature were determined. The formation of precipitates and their effects on the microstructure was studied by using OM, DSC and hardness measurements. The formation of precipitates varies the chemical composition of the alloys and thereby changes the shape memory Effect and Transformation temperature of the alloys. The investigation results are expected to benefit the applications of Cu-Al-Be SMA under different thermal conditions as a replacement of costly NiTinols.

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***Keywords* -** Shape Memory Alloys; Cu-Al-Be; Ageing; Vickers Hardness; DSC.

1. Introduction

Shape memory alloys (SMA) are the unique class of smart metallic materials which have an intrinsic ability to recover the predefined shape upon appropriate thermal or mechanical treatment without the residual strain. The distinct properties of SME, as well as pseudoelasticity, two-way shape memory effect, rubber-like behaviour and high damping capacity, are closely related to the thermoelastic martensitic transformation was explained by the researchers Hsu C A et al. (2005), Mallik U S et al. (2008) and Miyazaki S et al. (1989). Manosa LI et al. (1998) explains the recovery of strain with the thermal (one way shape memory effect) or mechanical treatment (pseudo-elasticity) is attributed to the thermoelastic martensitic transformation. Nitinols (Ni-Ti shape memory alloys) is one of the classical example unravelling the commercial potential of shape memory alloy applicability. Ni-Ti alloys are highly expensive, which restricts its applications to niche markets such as medical stents, industrial automation, aerospace and defence. Recently it is found that Cu based alloys like Cu-Al-Zn, Cu-Al-Mn, Cu-Al-Be also exhibit

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shape memory effect (SME). Balo S N et al. (2001), Chung C Y et al. (1998) and Feng Chen et al. (2009) explains as Cu based SMAs have been preferred since they have good memory properties, low production cost and ease of manufacturing. In these alloys, the SME is achieved through a thermoelastic martensitic transformation. Zuniga H F et al. (1995) explains in Cu-Al alloy, the disordered BCC, β, austenite phase, which is responsible for shape memory behaviour, is stable at high temperatures. Balo S Net al. (2002) and Chentouf S M et al. (2010) explains the small addition of Be into Cu-Al alloy brings down martensite transformation temperature extraordinarily without affecting β phase stability, and also favours the DO3 ordered structure in metastable austenite. Belkahla S et al. (1993) explains the addition of only 0.1 wt% of Be reduces the phase transformation temperature of this alloy by approximately 100^0C. The wide variations of transformation temperature with a small amount of Be addition make a Cu-Al-Be SMA scientifically interesting and technologically important. Wu M H et al. (2000) explains, this alloy has many interesting properties such as super-elasticity, an excellent capacity to absorb sound, vibration and mechanical waves, high mechanical strength, resistance to corrosion etc. In the present study, an attempt was made to study the effect of Ageing in the Cu-Al-Be SMA prepared by gravity die casting technology using induction melting. The transformation temperatures of the alloys showing the Shape memory effect were determined by using Differential Scanning Calorimetry (DSC) and the phases using optical microscope. The one way shape memory effect of this alloy was also verified by bend test. The SMAs have many technological applications. For the Cu-Al-Be alloy, a confirmed prior studies of Jurado M et al. (1997), Manosa LI et al. (1998) reveals the DO3 type transition. Chentouf S M et al. (2010) and Kuo H H et al. (2006) explains as precipitate formation was mainly responsible for shape memory effect deterioration, its absence in the martensitic matrix confirms the good shape memory characteristics of the alloy.

However, Low ageing resistance, coarse grain and poor thermal stability are some of the draw backs associated with it. The aim of the present study is to investigate aging of alloy above the austenite finish transformation temperature associated with formation of precipitates, variation in transformation temperature and Shape memory effect.

2.0 Experimental Procedure

Cu-Al-Be SMAs with 9 - 15 wt.% of aluminum and 0.4 - 3 wt.% of Beryllium were chosen for the present study, as the alloys exhibit β-phase at high temperatures and manifest shape memory effect on quenching to form martensite in this composition range. The alloys were prepared in such a way that, small pieces of pure copper, aluminum and beryllium cut from the respective metal ingots were taken in the right quantities to weigh 300 gm of the alloy and were melted together in an induction furnace. The molten alloy was poured into a cast iron mould of dimensions 150mm×100mm×5mm and allowed to solidify. The ingots were then homogenized at 900ºC for 4h. The compositions of the cast alloys were determined using an integrally coupled plasma-optical emission spectrophotometer. The alloy samples were then hot rolled at 900ºC to a thickness of 1 mm. The rolled samples were betatized for 30min at 900ºC and step quenched into boiling water (100ºC) and then quenched into a water bath at room temperature (~30ºC). The microstructure and morphology of martensites formed were studied using an optical microscope and compositional analysis was carried out for the samples. The prepared samples tested for Shape Memory effect by bend test, Feng Chen et al. (2009). The transformation temperatures were determined using a differential scanning calorimeter (DSC) by heating/cooling the samples at a rate of 10ºC/min. Then the alloys were subjected thermal ageing for different holding times ranging from 1 – 4 hours with varying temperatures. The microstructure change with the formation of precipitates was investigated using DSC. The effect of ageing on hardness of the alloys was determined using Zwick Rockwell hardness testing machine.

3.0 Results and Discussion

3.1 Compositional analysis

Cu-Al-Be shape memory alloys with composition given in Table1 were prepared using an induction furnace. The compositions of the cast alloys were determined using Perkin Elmer Integrally Coupled Plasma-Optical Emission Spectrophotometer (ICP-OES) which is capable of determining the compositions up to the second decimal place. For composition analysis 1 gram of the alloy sample taken from the middle portion of the homogenized ingots.

Table 1: Chemical compositions of the Cu-Al-Be alloys.

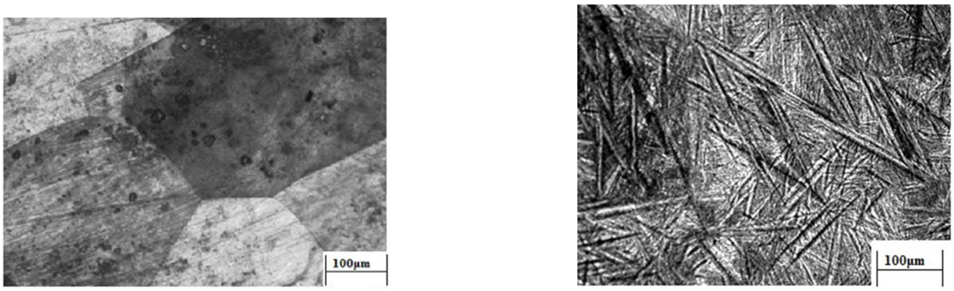
Alloy ID	Chemical compositions in (wt. %)		
	Cu	Al	Be
CAB[#] 1*	88.08	11.5	0.42
CAB 2	88.05	11.5	0.45
CAB 3	88.03	11.5	0.47
CAB 4	86.5	11.5	2.0
CAB 5	85.5	11.5	3.0

#CAB - Cu-Al-Be Ternary alloy
* Alloy Numbering

3.2. Microstructure

Samples were prepared for microstructral study using the emery sheets followed by cloth polishing with alumina paste to get very fine polished surface. Samples were etched using the etchant solution of K_2 Cr_2 O_7 - 8ml H_2 SO_4 - 2ml HCl - 100ml H_2 O. The microstructural studies of samples are carried out using Optical Microscope (Olympus-Japan).

The micrograph of austenite in room temperature and martensite micrograph structures are as in fig.1 (a) and (b). The as cast austenite microstructure and the formation of martensite variants on step quenching is as in Fig.1 (a) and (b). It can be observed that there is a complete transformation of austenite to martensite.



(a) ` (b)

Fig.1: Micrograph of the Cu-Al-Be alloy (a) Austenite (b) Lath Martensite.

3.3. Shape Memory Effect (SME)

The prepared specimens were subjected to the bend test to determine the strain recovery by shape memory effect. The SME obtained in percentage by bend test of the alloy is calculated by using the relation (θm /180°- θe) which is as in Table 2. (θe- angle of spring back, θm-angle recovered on heating).The alloys exhibit a strain recovery of 85 % to 100% by SME.

Table 2. Strain recovery by SME.

Sample	d (mm)	t (mm)	θ_e	θ_m	SME %
CAB 1	32	1	90	80	89
CAB 2	32	1	90	85	95
CAB 3	32	1	90	90	100
CAB 4	32	1	90	72	80
CAB 5	32	1	90	78	87

3.4 Transformation Temperature

Transformation Temperatures, i.e. Ms, M_f, As and A_f of the alloys were determined using in Differential Scanning Calorimeter under Nitrogen gas atmosphere, adopting a heating and cooling rate of 10^oC/min. About 0.75 mm to 1 mm thick specimens of 5 mm diameter was taken from the rolled, betatized and step quenched alloy samples. These specimens were polished using emery papers to obtain perfectly flat surfaces, so that they would be in good contact with the bottom surface of the specimen holder in the DSC. Fig. 2 gives the DSC curve for the alloy sample CAB3.

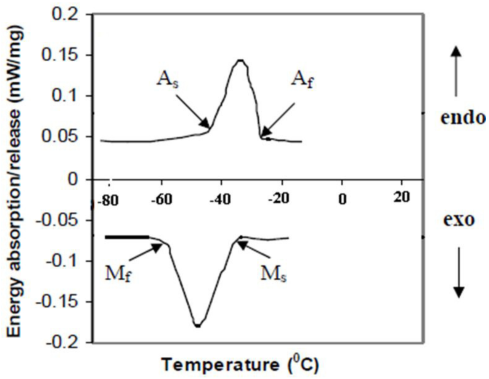


Fig.2. DSC plot of the Shape Memory Alloy Sample CAB 3

The phase transformation Temperatures of the samples which were subjected to ageing studies were determined by DSC after the ageing treatment at various temperatures. The Ms, M_f and As, A_f temperatures of the aged samples exhibits that the transformation temperatures of the aged samples varies with an increase in the ageing time. The exposure of the alloy for more duration leads to poor shape memory capability.

3.5 Ageing Behaviour of the Cu-Al-Be SMA

The samples are aged at 250^0C and 500^0C for 1h, 2h and 3h duration. The microstructrual studies, Variation in transformation temperatures was carried out using OM and DSC respectively. The precipitates formed were studied using EDAX and variation in hardness was determined using Zwick-Roell Vickers hardness tester.

3.5.1 Micro structural Analysis

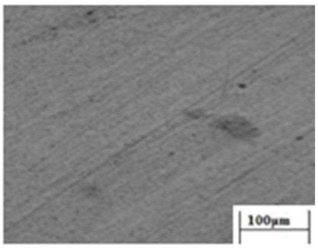


Fig.3 Optical micrograph of surface of alloy sample CAB 3: before ageing.

The micrograph of surface of the specimen before ageing is as in Fig.3. Micro structural studies of the specimen has been carried out under same ageing temperature for the different time interval. The small pieces of the prepared specimen cut from the thin sheet of the prepared Cu-Al-Be shape memory alloy, into four sets of sample. Each of these four sample sets were kept for one, two, three and four hour respectively inside the oven at 250^oC and 500^oC. All these aged specimens were tested under the microscope and microstructure of each were obtained and analyzed.

3.5.2 Ageing at 250 º C

The micrographs obtained after ageing the alloy specimens at 250^{0}C for 1, 2, 3 and 4 hour is as in Fig.4. It can be observed that, the precipitate size has increased with the increase in time of ageing. The microstructural analysis reveals that with the increase in the time of ageing the formation of precipitates is being increased.

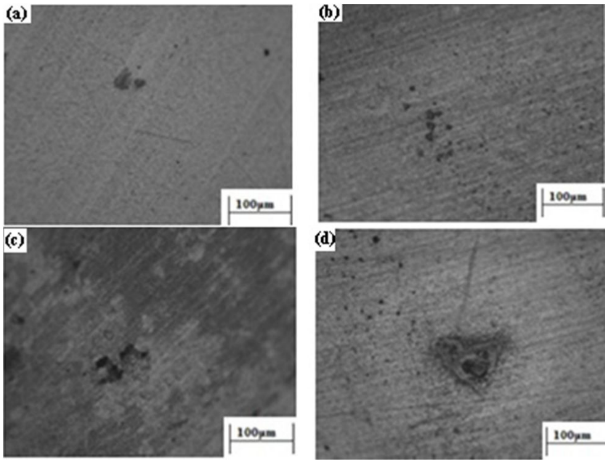


Fig.4. Optical micrographs of alloy sample CAB 3 ageing at 250 ºC: (a) after one hour ageing: (b) after two hour ageing: (c) after three hour ageing: (d) after four hour ageing.

3.5.3 Ageing at 500 ºC

Fig.5. shows the micrographs of the alloy specimen aged at 500^{0}C for 1, 2, 3 and 4 hour of duration. The denser and darker precipitates are observed in the specimens. At higher temperature and increase in the time of ageing the formation of precipitates increased.

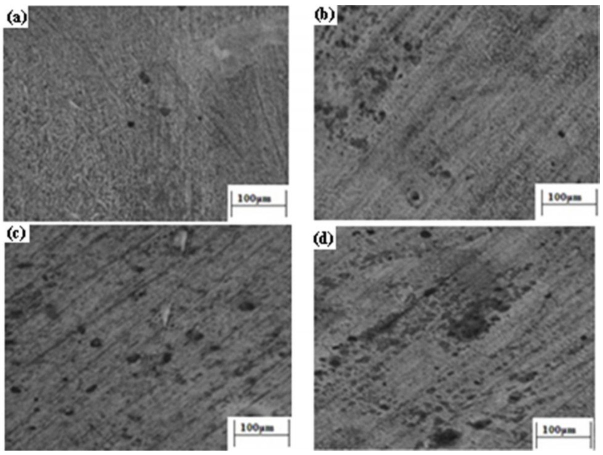


Fig.5. Optical micrographs of alloy sample CAB 2, ageing at 500 ºC (a) after one hour ageing: (b) after two hour ageing: (c) after three hour ageing: (d) after four hour ageing.

3.6 Transformation Temperature after Ageing

The phase transformation Temperatures of the samples which were subjected to ageing studies were determined by DSC. The Ms, M_f and As, A_f temperatures of the aged samples at various temperatures are as in table 3, it exhibits an increase in the transformation temperatures as the ageing time increases. The exposure of the alloy for more duration leads to poor shape memory strain recovery. The peaks of endothermic and exothermic profiles of DSC are as in Fig.6. It is observed that, after 1 hour ageing, both the phase transformation temperatures are is increased. After 2 hour ageing, the transformation temperatures are at maximum values.

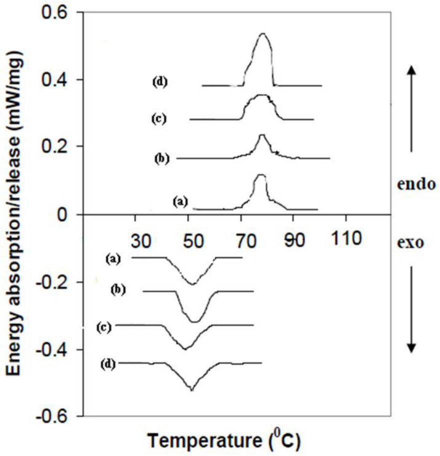


Fig.6. The DSC Curves (a)Ageing at 1hr (b) Ageing at 2h (c)Ageing at 3h (d)Ageing at 4 h.

Table 3. Transformation temperatures of SMA aged at 250^{0}C

Ageing Time	Transformation Temperature in ^{0}C			
	Ms	M_f	As	A_f
1	58.4	43.2	72.3	87.6
2	60.1	44.5	74.2	88.7
3	54.3	38.7	71.4	83.8
4	53.8	39.6	73.1	86.5

3.7 SME after Ageing

The strain recovery by SME of the alloys subjected to various ageing temperatures and time were determined by bend test. It was observed that with increase in the time and temperature, the strain recovery by SME is decreased due to the formation of precipitates. The formation of precipitates changes the composition of the alloy which thereby changes the SME of the alloy. The variation in strain recovery by SME after ageing at 250^{0}C for various duration is as in table 4.

Table 4. Variation in SME after bend test. (Before and after ageing at 250^{0}C)

Sample	SME %			
	Before Ageing	After 1 hr ageing	After 2 hr ageing	After 3 hr ageing
CAB 1	89	80	65	40
CAB 2	95	77	60	45
CAB 3	100	82	75	60
CAB 4	80	70	55	35
CAB 5	87	72	62	37

3.8 Micro Hardness Test

Micro hardness test was performed on the specimens which were subjected ageing to examine whether there is any change in the mechanical properties of the material when they are aged for different time duration. A load of 50 gram for 10 sec has been used for testing.

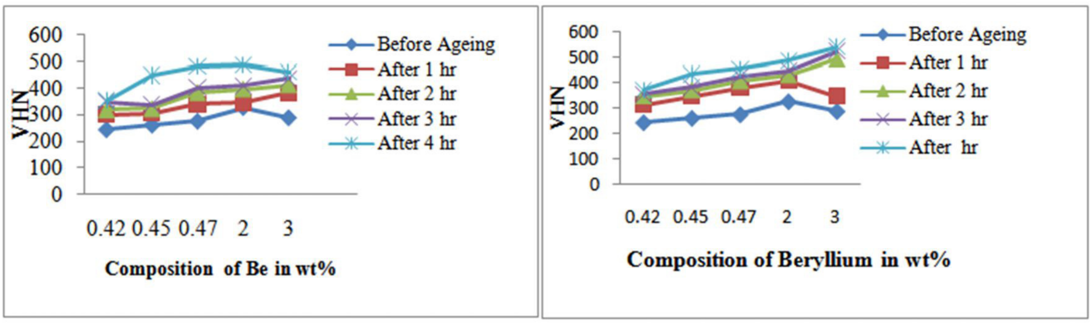
The variation of Vickers hardness of the heat treated samples at 250°C and 500°C with ageing time is shown in Fig7. (a) and (b). From the graph it is observed that the Vickers hardness of the alloy increases with increasing ageing duration. The formations of precipitates in the alloy is increased with increase in ageing time. The imperfections present in the alloy will move and fill the empty spaces at higher temperatures which solidify on cooling which hardens the alloy. The variation in hardness with variation in ageing time and temperature is as given in table 5 and 6.

Table.5 Variation in VHN of Cu-Al-Be SMA (Before and After Ageing for 250 ºC)

Alloy ID	Before Ageing	After 1 hr ageing	After 2 hr Ageing	After 3 hr Ageing	After 4 hr Ageing
CAB 1	243	299	317	345	353
CAB 2	260	306	322	336	447
CAB 3	274	339	383	401	480
CAB 4	325	345	396	407	487
CAB 5	287	381	412	435	460

Table.6. Variation in VHN of Cu-Al-Be SMA (Before and after ageing for 500 ºC)

Alloy ID	Before Ageing	After 1 hr Ageing	After 2 hr Ageing	After 3 hr Ageing	After 4 hr Ageing
CAB 1	243	311	345	353	371
CAB 2	260	345	370	381	435
CAB 3	274	376	405	423	453
CAB 4	325	405	429	447	487
CAB 5	287	345	493	524	540



(a) (b)

Fig.7. VHN v/s Composition of Be in wt% (a) Ageing at 250^{0}C (b) Ageing at 500^{0}C

Conclusions

- The Cu-Al-Be SMA's exhibits good SME (up to 100%) which varies with variation in chemical composition of the alloys.
- The Cu-Al-Be SMAs forms various precipitates on ageing.
- The formation of precipitates enhances with increase in the duration of ageing.
- The transformation temperatures increase with increase in the ageing time and temperature.
- The hardness of the alloys is increasing with increase in the ageing time and the amount of beryllium in the alloy as it forms a hard layer of beryllium oxide.
- The strain recovery by Shape Memory Effect decreases with the increase in the ageing time due to increase in the amount of precipitates.

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